THE CHLORINATION OF THE METHYL, ETHYL, ISOPROPYL, AND NORMAL PROPYL ESTERS OF MONOCHLOROACETIC ACID

A THESIS

Submitted in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry

by

Norman Hagood Horton

The Georgia School of Technology

Atlanta, Georgia

1942

THE CHLORINATION OF THE METHYL, ETHYL, ISOPROPYL, AND NORMAL PROPYL ESTERS OF MONOCHLOROACETIC ACID

Approved:

Date Approved by Chairman May 11, 1942

DISCLAIMER:

This document has been proofed.
All formatting is preserved from original document.

ACKNOWLEDGMENTS

On the completion of this work I wish to express my appreciation to Dr. H. M. Waddle who suggested and directed this problem. I also wish to thank the General Education Board, whose funds provided part of the equipment used in this work.

TABLE OF CONTENTS

LIST OF TABLES (CONT'D)

LIST OF FIGURES

THE CHLORINATION OF THE METHYL, ETHYL, ISOPROPYL, AND NORMAL PROPYL ESTERS OF MONOCHLOROACETIC ACID

PART I

HISTORY

A survey of the literature shows that no work has been published on the chlorination of the esters of monochloroacetic acid. Waddle[1] and Gayler[2], however, have studied the action of chlorine on the butyl and propyl esters of trichloroacetic acid. It seemed that the chlorination of some esters of monochloroacetic acid would throw additional light on the relative reactivity of hydrogen atoms attached to primary and secondary carbon atoms as well as to prepare some new chlorinated esters which might have some value as solvents.

PART II

PREPARATION OF THE ESTERS

The methyl, ethyl, isopropyl, and normal propyl esters of monochloroacetic acid were prepared by refluxing 5 moles of Merck's U.S.P. monochloroacetic acid with 10 moles of the alcohol and 50 cc concentrated sulfuric acid for about 8 hours. The excess alcohol was then distilled

---

[1] Waddle, H.M., J. Am. Chem. Soc., 61 3361 (1939)

[2] Gayler, C.W., ibid., 63 3358 (1940)

off and the crude ester was washed thoroughly with water. The crude ester was then washed with 5 per cent sodium carbonate solution to remove any traces of free acid. The ester was finally washed with water, dried over anhydrous calcium chloride, and distilled through a 50 cm Vigreaux column. The ester thus obtained was again distilled and the middle cut of the pure fraction was used for the chlorination.

All molar refractions were determined by substituting the experimental index of refraction and density in the Lorinz and Lorentz equation.[3]

$$M_D = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{m}{d}$$

where n is the index of refraction, d the density and m the molecular weight of the compound. The value thus obtained is listed in the tables under the heading, M_D found. The calculated molar refractions were obtained from the empirically deduced atomic and structural refractive constants given by Smiles.[4]

Table I shows the physical properties of the esters which were prepared. The literature values given in the table were taken from Beilstein.[5]

---

[3]Shriner and Fuson, Identification of Organic Compounds, 2nd Ed., John Wiley and Sons, p.107 (1940)

[4]Smiles, The Relation Between Chemical Constitution and Some Physical Properties, Longmans, Green and Co. (1919)

[5]Beilstein, Handbuch der Organischen Chemie, 4th Ed., Vol.II, p.198

TABLE I

Physical Constants of Esters Prepared

Ester of Chloroacetic Acid	Batch Number	Boiling Point 760 mm Found	Boiling Point 760 mm Lit.	D_4^{20} Found	D_4^{20} Lit.	n_D^{20} Found	n_D^{20} Lit.	M_D Found	M_D Calc'd	Per Cent Yield
Methyl	1	128-9	129.6	1.2308	1.2358	1.4213	1.42207	22.84	22.68	45.5
Methyl	2	128-9	129.6	1.2327	1.2358	1.4211	1.42207	22.85	22.68	51.1
Methyl	1A	128-9	129.6	1.2344	1.2358	1.4221	1.42207	22.34	22.68	52.5
Ethyl	1	142	143.5	1.1505	1.1520	1.4211	1.42162	26.91	27.29	66.6
Ethyl	2	142	143.5	1.148	1.1520	1.4210	1.42162	27.06	27.29	51.5
Ethyl	2A	143	143.5	1.1510	1.1520	1.4225	1.42162	27.29	27.29	55.5
Ethyl	3	142	143.5	1.1507	1.1520	1.4212	1.42162	26.94	27.29	----
Iso Propyl	1	148	149	1.0866	$1.0944(\frac{15}{4})$	1.4192	-------	31.75	31.89	48.7
Iso Propyl	2	148	149	1.087	$1.0944(\frac{15}{4})$	1.4192	-------	31.72	31.89	21.2
n. Propyl	1	161-2	161	1.102	1.1050	1.4250	1.42557	31.66	31.89	71.0
n. Propyl	2	160	161	1.1010	1.1050	1.4250	1.42557	31.69	31.89	48.5
n. Propyl	3	161	161	1.1025	1.1050	1.4250	1.42557	31.43	31.89	----

PART III

CHLORINATION OF THE ESTERS

Each ester was chlorinated by passing gaseous chlorine through the ester at 120°C. in the presence of a 150 watt light bulb placed 5 cm from the chlorinating flask. The chlorination temperature was selected as 120°C. because of the work of Waddle and Gayler[1,2] who found that the trichloroacetates chlorinated readily at that temperature.

The chlorinating flask was a one-liter boiling flask with the female part of a number 24/40 standard taper ground glass joint sealed to the central neck. Three additional necks of 7/16 inch diameter were symetrically located around the central neck. The male part of the ground glass joint was sealed to a piece of glass tubing which served as a guide and a bearing for a mechanical stirrer.

The source of chlorine was a tank of commercial chlorine. The chlorine was passed through a concentrated sulfuric acid washing bottle[6] and a flowmeter containing concentrated sulfuric acid before entering the flask. The outlet gases were passed through a spiral condenser and finally the unreacted chlorine and hydrogen chloride were absorbed in a water trap.

A digram of the chlorinating apparatus is shown by Gayler.[7] A constant temperature of 120°C. was maintained during chlorination by means of an oil bath equipped with an immersion electrical heater and

---

[6] McKenny, Ind. Eng. Chem., Anal. Ed., 6 258 (1934)

[7] Gayler, Georgia School of Technology, Master's Thesis, p.6A (1940)

thermoregulator operated by a thermionic relay.[8]

The esters were chlorinated in duplicate batches of approximately 2 gram moles each. A typical chlorination was carried out as follows: The ester to be chlorinated was placed in the chlorinating flask, the flask was connected to the water trap, and the stirrer was started. The oil bath and ester were brought to working temperature, and the chlorine tank was opened. The pressure of the chlorine was adjusted until the sulfuric acid in the flowmeter showed a reading of about 20 mm which corresponded to a rate of flow of approximately 20 grams per hour. The amount of chlorine absorbed was determined by weighing the flask. Chlorination was discontinued when the ester absorbed a weight of chlorine corresponding to mono chloro substitution. The tables II through XII give the chlorination data for each batch.

The chlorinated methyl chloroacetate batch I was ruined by sodium hydroxide solution sucking back into the chlorinating flask. Batch II of ethyl chloroacetate was lost due to breakage of the chlorinating flask. Ethyl chloroacetate batch I and normal propyl chloroacetate batch I decomposed during the summer of 1941. This decomposition was probably brought about by the impurities present due to the solvent action of the esters on a rubber stopper in the central neck of the flask. This stopper was replaced with a ground glass joint and all subsequent chlorination products were stable and water clear.

---

[8] Mudy and Fugassi, Ind. Eng. Chem., Anal. Ed., 12 757 (1940)

TABLE II

Chlorination of Methyl Chloroacetate Batch I

Weight of ester = 217 grams = 2 moles

Weight of chlorine absorbed after 3 hours -- 18 grams

Weight of chlorine absorbed after 5 hours -- 27 grams

Sodium hydroxide solution was sucked back into the flask. Batch ruined.

TABLE III

Chlorination of Methyl Chloroacetate Batch 2

Weight of ester = 217 grams = 2 moles

Weight of chlorine absorbed after 3 1/2 hours --- 41 grams

Weight of chlorine absorbed after 6 hours ------- 52 grams

Weight of chlorine absorbed after 8 hours ------- 60.5 grams

Weight of chlorine absorbed after 10 hours ------ 62.5 grams

Weight of chlorine absorbed after 11 3/4 hours -- 65 grams

Weight of chlorine absorbed after 13 1/2 hours -- 69 grams

Weight of chlorine absorbed after 17 1/2 hours -- 72 grams

TABLE IV

Chlorination of Methyl Chloroacetate Batch 1A

Weight of ester = 217 grams = 2 moles

Weight of chlorine absorbed after 5 hours ------ 39 grams

Weight of chlorine absorbed after 9 1/2 hours -- 48 grams

Weight of chlorine absorbed after 11 1/2 hours - 57 grams

Weight of chlorine absorbed after 14 hours ----- 66 grams

Weight of chlorine absorbed after 15 1/2 hours -- 69 grams

Weight of chlorine absorbed after 15 3/4 hours -- 72 grams

TABLE V

Chlorination of Ethyl Chloroacetate Batch 1

Weight of ester = 245 grams = 2 moles

Weight of chlorine absorbed after 4 hours -------- 43 grams

Weight of chlorine absorbed after 6 hours -------- 61 grams

Weight of chlorine absorbed after 7 hours 10 min. - 69.5 grams

Weight of chlorine absorbed after 7 1/2 hours ---- 71 grams

TABLE VI

Chlorination of Ethyl Chloroacetate Batch 2A

Weight of ester = 245 grams = 2 moles

Weight of chlorine absorbed after 5 hours ------ 56 grams

Weight of chlorine absorbed after 6 1/2 hours -- 60 grams

Weight of chlorine absorbed after 8 hours ------ 71 grams

TABLE VII

Chlorination of Ethyl Chloroacetate Batch 3

Weight of ester = 226.5 grams = 1.85 moles

Weight of chlorine absorbed after 4 hours ---------- 35.5 grams

Weight of chlorine absorbed after 6 hours 20 min. ------- 56.5 grams

Weight of chlorine absorbed after 7 hours 30 min. ------- 64.5 grams

TABLE VIII

Chorination of Isopropyl Chloroacetate Batch 1

Weight of ester = 273 grams = 2 moles

Weight of chlorine absorbed after 5 3/4 hours ------ 49 grams

Weight of chlorine absorbed after 7 1/4 hours ------ 63 grams

Weight of chlorine absorbed after 8 1/2 hours ------ 72 grams

TABLE XI

Chlorination of Isopropyl Chloroacetate Batch 2

Weight of ester = 230 grams = 1.67 moles

Weight of chlorine absorbed after 4 1/2 hours ------ 39.5 grams

Weight of chlorine absorbed after 6 1/2 hours ------ 51.5 grams

Weight of chlorine absorbed after 7 1/4 hours ------ 57.5 grams

Weight of chlorine absorbed after 7 1/2 hours ------ 59.5 grams

TABLE X

Chlorination of Normal Propyl Chloroacetate Batch 1

Weight of ester = 273 grams = 2 moles

Weight of chlorine absorbed after 3 1/2 hours ------ 38 grams

Weight of chlorine absorbed after 6 hours ---------- 66.5 grams

Weight of chlorine absorbed after 6 1/2 hours ------ 71 grams

TABLE XI

Chlorination of Normal Propyl Chloroacetate Batch 2

Weight of ester = 273 grams = 2 moles

Weight of chlorine absorbed after 4 hours ------ 40.5 grams

Weight of chlorine absorbed after 6 1/2 hours -- 68.5 grams

Weight of chlorine absorbed after 7 hours ------ 71 grams

TABLE XII

Chlorination of Normal Propyl Chloroacetate Batch 3

Weight of ester = 273 grams = 2 moles

Weight of chlorine absorbed after 4 hours ------ 27.8 grams

Weight of chlorine absorbed after 7 hours ------ 52.3 grams

Weight of chlorine absorbed after 8 1/2 hours -- 64.8 grams

Weight of chlorine absorbed after 9 1/4 hours -- 70.3 grams

PART IV

APPARATUS AND PROCEDURE FOR SEPARATING THE CHLORINATED ESTERS

The compounds contained in the mixture of chlorinated esters were separated by fractional distillation under reduced pressure. The fractionating column was of the partial take off, total reflux, packed column variety as decribed by Waddle and Adkins.[10]

A constant pressure of 17 mm. of mercury was maintained by means of a flutter valve operated by a thermionic relay circuit.[11] The pot heat was controled by a De Khotinsky thermoregulator and a duplicate relay circuit.

A diagram of the fractionating column and accessories is found in the work of Gayler.[12]

The distillations were carried out in the usual manner as described by Morton.[13] The chlorinated ester was placed in the usual distilling flask and the dissolved hydrogen chloride was removed by reducing the pressure on the column by means of a water aspirator. After removal of the hydrogen chloride the column was connected to the vacuum pump and the pot heat regulated until moderate refluxing occured in the side arm of the column. The partial take off stopcock was then turned until a

---

[10] Waddle and Adkins, J. Am. Chem. Soc., 61 3361 (1939)

[11] Rudy and Fugassi, Ind. Eng. Chem., Anal. Ed. 12 757 (1940)

[12] Gayler, Georgia School of Technology, Master's Thesis, p.9a (1940)

[13] Morton, Labratory Technique in Organic Chemistry, p.81. McGraw Hill (1938)

ratio of 1 drop taken off to 40 to 60 drops returning to the still was obtained. This ratio was maintained throughout the distillation. During the distillation the temperature of the dead air space surrounding the column was kept 5 to 10° below the reflux temperature. Each distillation required from 60 to 100 hours.

Tables XIII through XX give the fractionation data for each batch of chlorinated ester.

TABLE XIII

Fractionation of Chlorinated Methyl Chloroacetate Batch 2

Cut Number	Distillation Temperature 17 mm	Pot Temperature	Column Temperature	Weight of Cut	Total Weight	n_D^{20}
1.	37-39°	84°	35°	2 g	2 g	
2.	39-40	85	35	2.5	4.5	
3.	40-41	90	35	18.5	23	
4.	41-43	94	35	7.5	30.5	
5.	43-47	95	36	7.0	37.5	
6.	47-50	100	34	21.5	59.0	
7.	50-57	105	40	9.0	68.0	
8.	57-72	110	51	4.0	72.0	
9.	72-75	110	60	4.5	76.5	
10.	75-76	110	60	3.5	80.0	
11.	76-77	115	71	176.0	256.0	1.4580
	Residue			21.5		
Cuts 1-10 were placed in smaller flask and refractionated						
1.	37-39°	85°	33°	.5 g	.5 g	1.4409
2.	39-40	92	34	1.1	1.6	1.4282
3.	40-41	95	35	9.5	11.1	1.4239
4.	41-42	95	36	8.0	19.1	1.4240
5.	42-43	95	36	4.9	24.0	1.4258
6.	43-44	95	35	2.3	26.3	1.4277
7.	44-45	97	41	3.4	29.7	1.4306
8.	45-46	98	42	3.0	32.7	1.4334

TABLE XIII (Continued)

Cut Number	Distillation Temperature 17 mm	Pot Temperature	Column Temperature	Weight of Cut	Total Weight	n_D^{20}
9.	46-47°	98°	42°	2.4 g	35.1 g	1.4362
10.	47-48	98	40	4.0	39.1	1.4391
11.	48-49	98	40	5.2	44.3	1.4413
12.	49-50	110	43	10.0	54.3	1.4431
13.	50-51	120	44	2.5	56.8	
14.	51-53	120	44	1.2	58.0	
		Residue		9.0		

TABLE XIV

Fractionation of Chlorinated Methyl Chloroacetate Batch 1A

Cut Number	Distillation Temperature 17 mm	Pot Temperature	Column Temperature	Weight of Cut	Total Weight	n_D^{20}
1.	42-44°	90°	38°	7 g	7g	1.4260
2.	44-45	90	38	7.3	14.3	1.4279
3.	45-47	90	38	3.5	17.8	1.4292
4.	47-48	90	38	4.0	21.8	1.4327
5.	48-50	95	38	5.8	27.6	1.4369
6.	50-53	100	45	5.6	33.2	1.4400
7.	53-57	105	48	5.4	38.6	1.4428
8.	57-74	110	57	4.0	42.6	1.4468
9.	74-78	110	63	5.0	47.6	1.4531
10.	78-80	110	75	201.8	249.4	1.4583
		Residue		8.8		

TABLE XV

Fractionation of Chlorinated Ethyl Chloroacetate Batch 2A

Cut Number	Distillation Temperature 17 mm	Pot Temperature	Column Temperature	Weight of Cut	Total Weight	n_D^{20}
1.	36-40°	75°	35°	1.9 g	1.9 g	
2.	40-47	75	--	0.6	2.5	
3.	47-49	80	--	2.8	5.3	
4.	49-50	85	--	1.1	6.4	
5.	50-51	95	42	14.9	21.3	1.4222
6.	51-53	95	45	9.7	31.0	1.4240
7.	53-55	95	45	0.8	31.8	
8.	55-60	95	45	1.4	33.2	
9.	60-62	95	45	1.0	34.2	
10.	62-67	95	47	2.2	36.4	
11.	67-76	100	67	4.3	40.7	
12.	76-77	100	67	8.3	49.0	
13.	77-79	100	70	91.3	140.3	1.4476
14.	79-90	120	75	0.7	141.0	
15.	90-97	120	80	1.9	142.9	
16.	97-99	120	90	2.4	145.3	
17.	99-100	125	91	3.3	148.6	
18.	100-102	125	93	62.1	210.7	1.4659
	Residue			22.1		

TABLE XVI

Fractionation of Chlorinated Ethyl Chloroacetate Batch 3

Cut Number	Distillation Temperature 17 mm	Pot Temperature	Column Temperature	Weight of Cut	Total Weight	n_D^{20}
1.	25-39°	--	--	1.5 g	1.5 g	
2.	39-50.5	95°	37°	3.4	4.9	
3.	50.5-52	100	41	16.7	21.6	1.4218
4.	52-66	100	56	6.9	28.5	
5.	66-76	105	56	3.8	32.3	
6.	76-77	105	70	2.3	34.6	
7.	77-78	105	72	65.7	100.3	1.4471
8.	78-79	---	--	46.9	147.2	1.4472
9.	79-85	125	79	7.5	154.7	
10.	85-97	125	80	3.3	158.0	
11.	97-100	130	83	8.4	166.4	
12.	100-102	---	--	51.4	217.8	1.4649

TABLE XVII

Fractionation of Chlorinated Isopropyl Chloroacetate Batch 1

Cut Number	Distillation Temperature 17 mm	Pot Temperature	Column Temperature	Weight of Cut	Total Weight	n_D^{20}
1.	up to 29°	55°	33°	27.4 g	27.4 g	1.4488
2.	29-38	70	38	2.3	29.7	1.4435
3.	38-51	70	38	2.2	31.9	1.4315
4.	51-53	70	43	2.5	34.4	1.4224
5.	53-54	70	43	1.4	35.8	1.4223
6.	54-55	70	53	55.6	91.4	1.4198
7.	55-56	--	--	39.2	130.6	1.4200
8.	56-59	90	54	4.1	134.7	1.4238
9.	59-62	100	55	3.2	137.9	1.4283
10.	62-67	105	60	2.6	140.5	1.4333
11.	67-74	110	68	5.6	146.1	1.4568
12.	74-75	110	69	2.9	149.0	1.4750
13.	75-76	115	71	4.8	153.8	1.4832
14.	76-80	115	80	13.2	167.0	1.4840
15.	80-85	115	78	3.9	170.9	1.4845
16.	85-90	115	80	1.8	172.7	1.4848
17.	90-95	120	81	2.7	175.4	1.4765
18.	95-99	120	--	3.8	179.2	1.4645
19.	99-101	120	--	8.6	187.8	1.4538
20.	101-102	120	91	69.0	256.8	1.4568
	Residue			18.7		

TABLE XVIII

Fractionation of Chlorinated Isopropyl Chloroacetate Batch 2

Cut Number	Distillation Temperature 17 mm	Pot Temperature	Column Temperature	Weight of Cut	Total Weight	n_D^{20}
1.	up to 52°	60°	31°	--	--	
2.	52-54	75	40	2.4 g	2.4 g	1.4218
3.	54-55	75	42	61.8	64.2	1.4200
4.	55-56	85	43	4.0	68.2	1.4222
5.	56-67	105	52	8.8	77.0	1.4318
6.	67-72	110	55	2.6	79.6	1.4575
7.	72-74	115	64	1.6	81.2	1.4762
8.	74-75	120	67	7.9	89.1	1.4852
9.	75-76	120	69	4.7	93.8	1.4872
10.	76-77	120	68	2.0	95.8	1.4865
11.	77-78	120	69	0.9	96.7	1.4877
12.	78-95	120	88	8.9	105.6	1.4807
13.	95-100	120	89	8.4	114.0	1.4600
14.	100-101	120	85	64.7	178.7	1.4568
	Residue			10.1		

TABLE XIX

Fractionation of Chlorinated Normal Propyl Chloroacetate Batch 2

Cut Number	Distillation Temperature 17 mm	Pot Temperature	Column Temperature	Weight of Cut	Toatl Weight	n_D^{20}
1.	60-63°	100°	50°	2.0 g	2.0 g	1.4261
2.	63-64	100	50	24.7	26.7	1.4251
3.	64-65	100	56	7.1	33.8	1.4256
4.	65-66	100	56	4.2	38.0	1.4267
5.	66-80	120	72	2.6	40.6	1.4303
6.	80-85	120	77	3.1	43.7	1.4380
7.	85-88	120	77	3.2	46.9	
8.	88-89	120	77	7.0	53.9	
9.	89-90	120	77	6.2	60.1	1.4479
10.	90-91	120	77	2.9	63.0	1.4476
11.	91-93	120	88	6.4	69.4	1.4493
12.	93-96	120	88	3.9	73.3	1.4506
13.	96-100	120	88	7.8	81.1	1.4523
14.	100-101	120	90	53.2	134.3	1.4562
15.	101-102	125	93	31.0	165.3	1.4575
16.	102-108	130	93	9.6	174.9	1.4591
17.	108-113	130	98	11.1	186.0	1.4640
18.	113-115	133	95	12.6	198.6	1.4656
19.	115-116	133	95	71.1	269.0	1.4640
20.	116-125	140	95	5.1	274.1	1.4621
21.	125-127	---	--	7.5	281.6	1.4732

TABLE XX

Fractionation of Chlorinated Normal Propyl Chloroacetate Batch 3

Cut Number	Distillation Temperature 17 mm	Pot Temperature	Column Temperature	Weight of Cut	Total Weight	n_D^{20}
1.	63-64°	100°	50°	43.0 g	43.0 g	1.4253
2.	64-82	---	--	4.0	47.0	
3.	82-84	---	--	1.7	48.7	
4.	84-87	110	60	2.0	50.7	
5.	87-88	110	60	7.2	57.9	
6.	88-89	---	70	8.3	66.2	1.4487
7.	89-93	110	70	9.1	75.3	
8.	93-98	115	--	5.5	80.8	
9.	98-99	120	--	5.6	86.4	
10.	99-100	---	--	5.8	92.2	
11.	100-101	---	--	68.1	150.3	1.4567
12.	101-102	---	--	13.2	163.5	
13.	102-112	150	98	16.0	179.5	
14.	112-115	---	--	17.3	196.8	
15.	115-	150	105	61.7	258.5	1.4639

PART V (A)

IDENTIFICATION OF THE COMPOUNDS PRODUCED BY THE CHLORINATION OF THE ESTERS

The compounds produced by chlorinating the esters were located by plotting rectification curves from the fractionation data given in tables XIII through XX. From these curves the approximate boiling points of the compounds were obtained and the fractions containing the pure compounds were saved.

Each pure fraction which did not decompose with water, was washed successively with water, 5 per cent sodium carbonate solution, and water, dried over anhydrous calcium chloride and distilled through a 10 inch Widmer type column at 17 mm. Those fractions which decomposed with water were distilled without washing. These purified fractions were then analyzed for chlorine by the method of Stepanow[14] as outlined by Kamm.[15]

During the fractionation of each ester a low boiling material collected in the dry ice trap which, when distilled at atmospheric pressure, boiled at 106°C. This material reacted violently with water, had a very irritating odor, and reacted with ammonia to give a white crystalline compound which melted at 119°C. It reacted with aniline to give a compound which melted at 133°C. Chloroacetamide melts at 119° and chloroacetanilde at 134.[16]

---

[14] Stepanow, Ber., 39 4056 (1906)

[15] Kamm, Qualitive Organic Analysis, 2nd Ed., p.200, John Wiley and Sons (1938)

[16] Shriner and Fuson, Identification of Organic Compounds, 2nd Ed., p.179, John Wiley and Sons (1940)

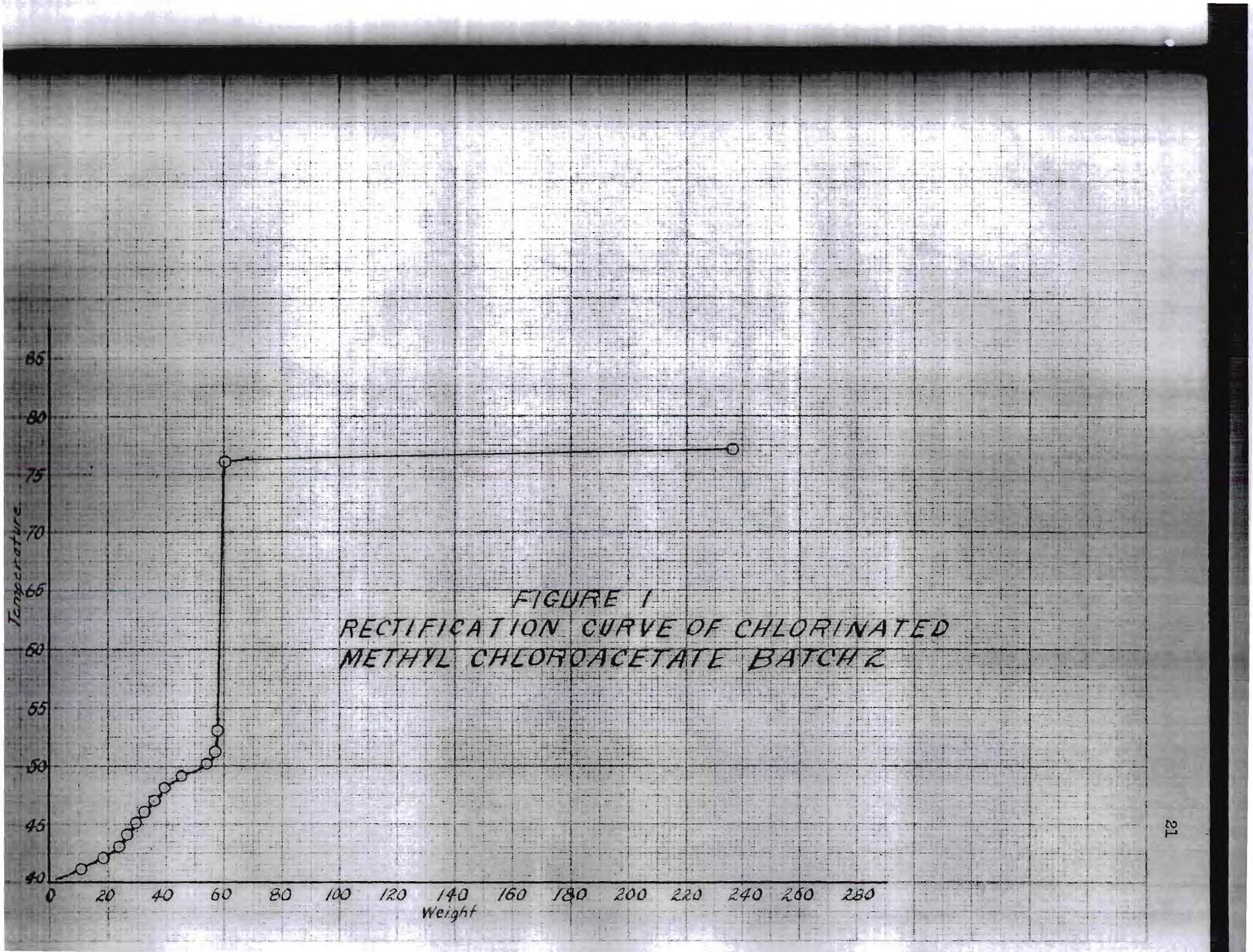


FIGURE 1
RECTIFICATION CURVE OF CHLORINATED METHYL CHLOROACETATE BATCH 2

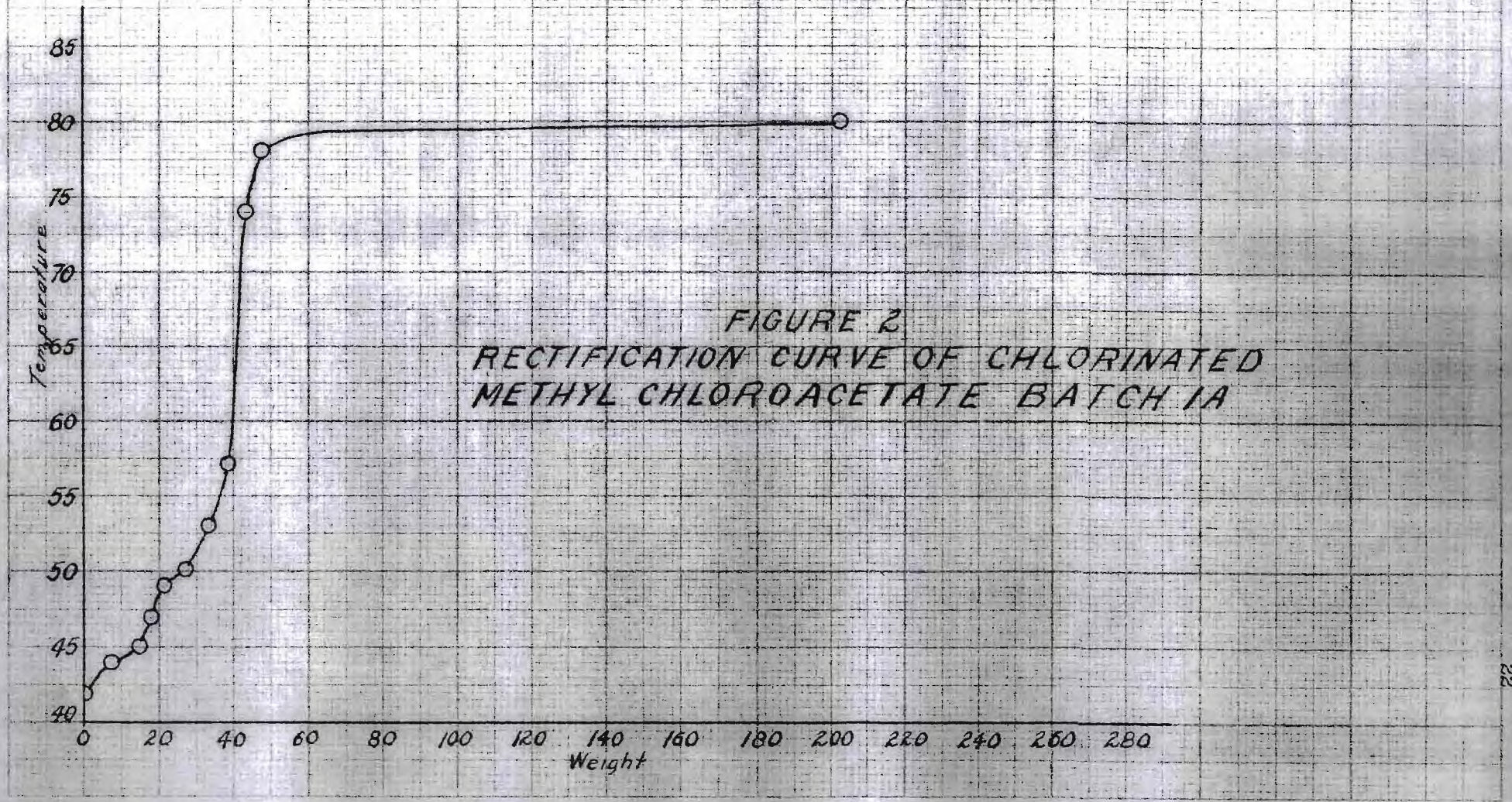


FIGURE 2
RECTIFICATION CURVE OF CHLORINATED METHYL CHLOROACETATE BATCH IA

The boiling point of chloroacetyl chloride is 105°C.[17]

It was therefore concluded that this material was chloroacetyl chloride and was produced by the chlorinolysis of the ester according to the following equation:-

$$R-\underset{H}{\overset{H}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2Cl \xrightarrow{Cl_2} \left[\underset{H}{\overset{H}{RC}}-O-Cl\right] \rightarrow RCHO + HCl + Cl-\overset{O}{\overset{\|}{C}}-CH_2Cl$$

The aldehydes which should have been formed according to the above reaction were not isolated. All of the aldehydes to be expected from the chlorination of the esters studied, however, are low boiling and polymerize readily in the presence of acids. It is very probable that the aldehydes were lost by being boiled off at the high chlorination temperature, or were polymerized to high boiling materials which were left in the residue when the esters were fractionated.

PART V (B)

PRODUCTS OBTAINED BY CHLORINATING METHYL CHLOROACETATE

An inspection of tables XIII and XIV and figures 1 and 2 shows one main fraction which had a boiling point of approximately 76°C at 17 mm. When further purified this compound from Batch II had the following properties:-

Color ------ water clear

Odor ------- sharp

---

[17] Shriner and Fuson, Identification of Organic Compounds, 2nd Ed., p.179, John Wiley and Sons (1940)

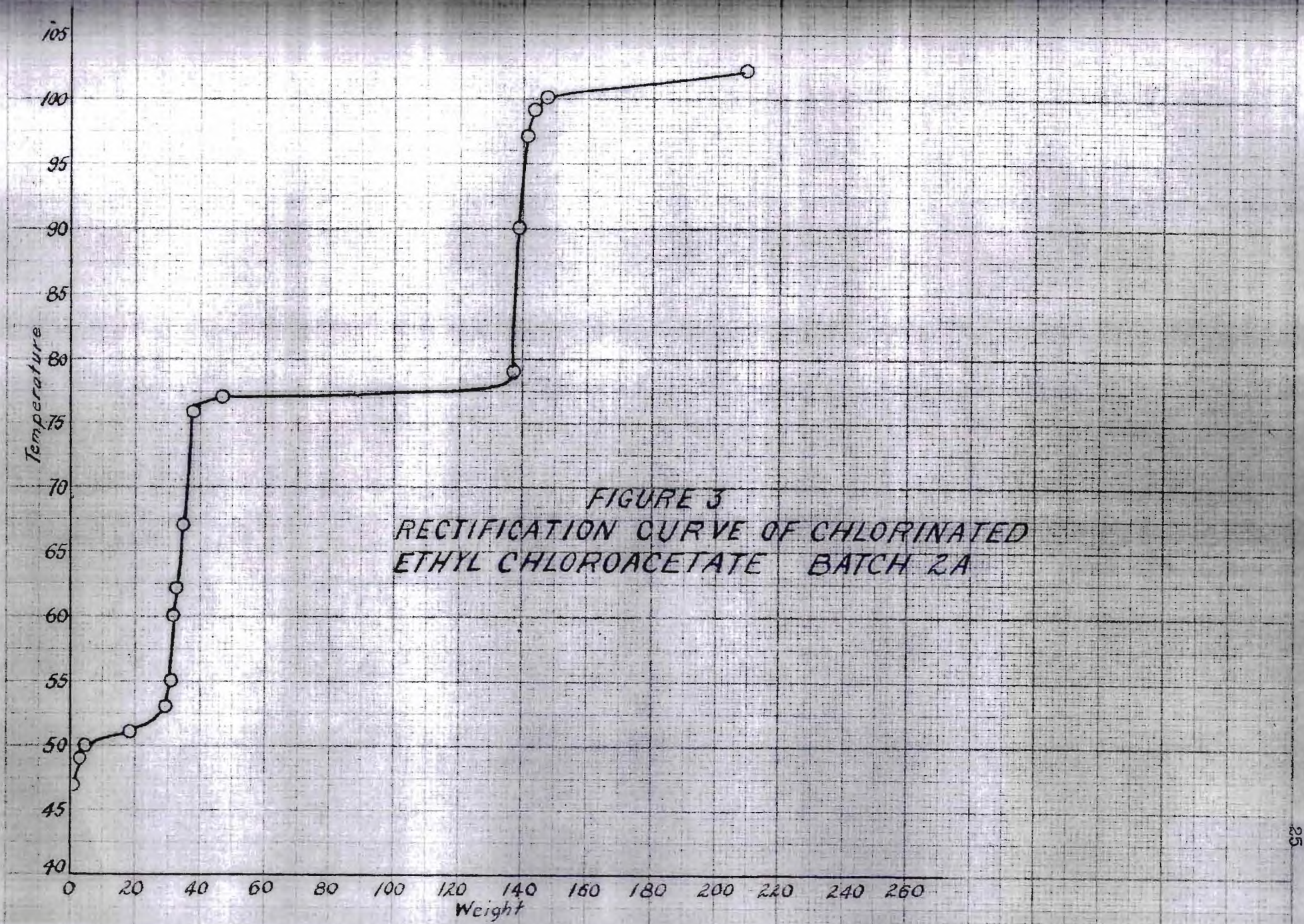


FIGURE 3
RECTIFICATION CURVE OF CHLORINATED ETHYL CHLOROACETATE BATCH 2A

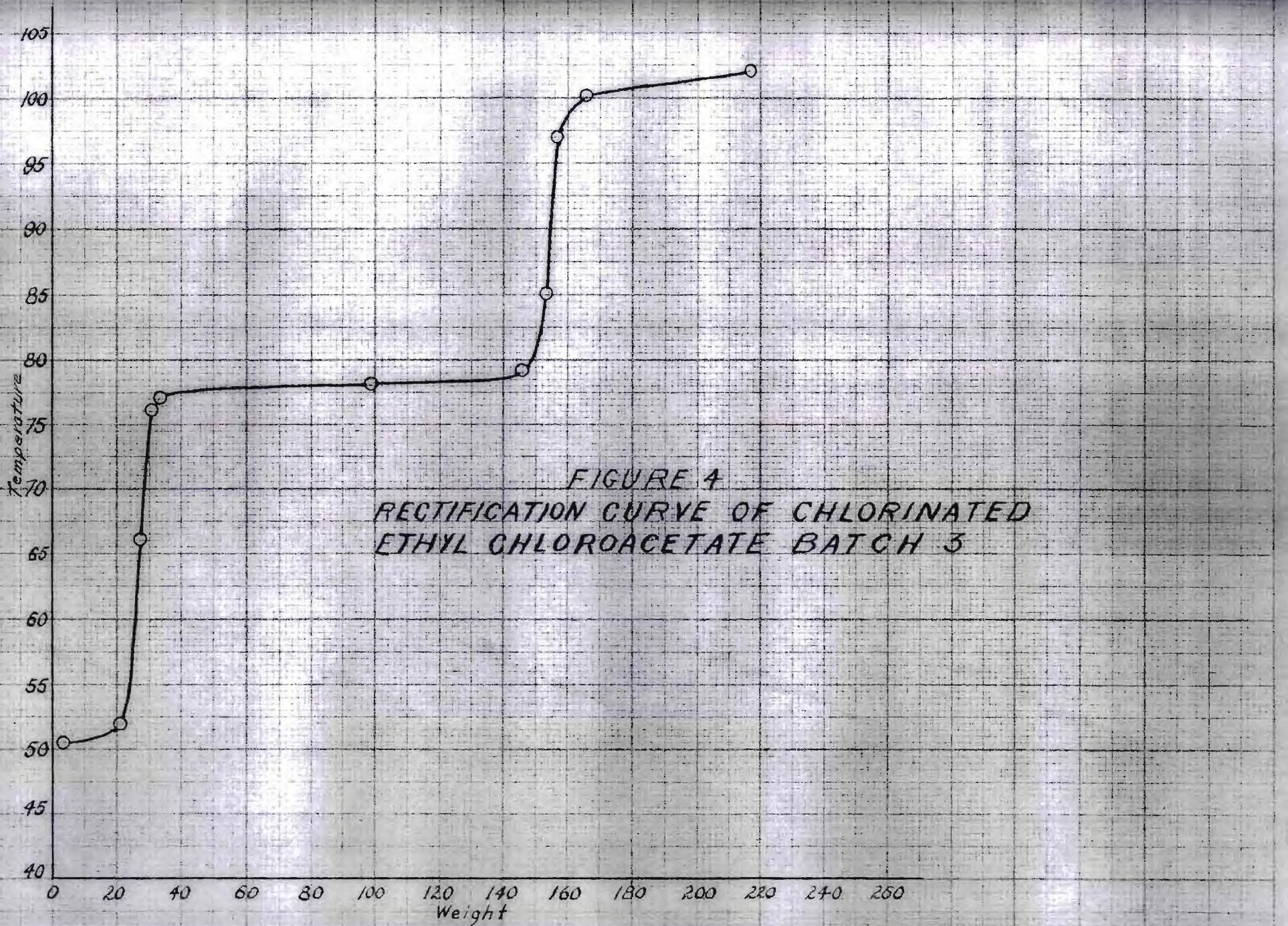
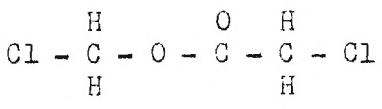


FIGURE 4
RECTIFICATION CURVE OF CHLORINATED
ETHYL CHLOROACETATE BATCH 3



The yield of chloromethyl chloroacetate was 70 pre cent for batch 1A and 61.5 per cent for batch 2.

Beilstein[20] gives the following properties for chloromethyl chloroacetated:-

Boiling point at 22 mm. ----- 82-85°C

D^{18} ---------- 1.420

PART V (C)

PRODUCTS OBTAINED BY CHLORINATING ETHYL CHLOROACETATE

An inspection of tables XV and XVI and figure 3 and 4 reveals three main fractions which result from chlorinating ethyl chloroacetate. These fraction have the following approximate boiling points at 17 mm.

Highest boiling fraction -------- 101°C

Next highest boiling fraction --- 77.5°C

Lowest boiling fraction --------- 51°C

The highest boiling fraction after washing and redistillation had the following properties:-

Color ----- water clear

Odor ------ slightly sweet, pleasant

Boiling point at 17 mm. ------ 100-101°C

---

[20]Beilstein, Handbuch der Organische Chemie, 4th Ed., Vol.2, p.198

	Batch 2A		Batch 3	
n_D^{20}	1.4650		1.4649	
D_4^{20}	1.3758		1.3760	
	Found	Calc'd for Dichloro Compound	Found	Calc'd for Dichloro Compound
M_D	32.27	32.24	32.27	32.35
% Cl	46.54	45.50	-----	-----
% Yield	19.7%		17.7%	

This compound reacted with concentrated ammonium hydroxide to yield chloroacetamide, melting point 119°C. The chloroacetamide was filtered off and the filtrate was extracted with ether for about 10 hours in a continuous extraction apparatus.[21] The ether was then distilled off and the residual liquid cooled in an ice bath. The additional chloroacetamide which separated out was filtered off and the filtrate distilled through an 8 inch Widmer type column. A main fraction was obtained from this distillation which had a boiling point of 125-128°C. This cut, when re-distilled in a smaller column, produced a liquid containing chlorine and had the following properties:-

Boiling point ------- 128°

n_D^{20} ---------- 1.4455

D_4^{20} ---------- 1.2045

Heilbron[22] gives the following physical properties for ethylene chlorohydrin

Boiling point ---- 128.6°C

---

[21] Morton, Labratory Technique in Organic Chemistry, p.206, McGraw Hill (1938)

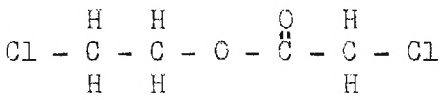
[22] Heilbron, Dictionary of Organic Compounds, Vol.2, p.29, Oxford University Press (1936)

n_D^{20} ------- 1.44189

D_4^{20} ------- 1.1988

No solid derivatives are listed. The molar refraction obtained experimentally was 17.79. The calculated value for ethylene chlorohydrin is 17.78.

Evidently, then, since the compound gave chloroacetamide and ethylene chlorohydrin on treatment with concentrated ammonium hydroxide, the compound had the following structure:-



Which is the structure of β chloroethyl chloroacetate.

Beilstein[23] lists this compound and gives the following physical property:-

D ---------- 1.317

The fraction which boiled at 51°C at 17 mm. had the following physical properties:-

	Batch 2	Batch 3
n_D^{20}	1.4222	1.4218
D_4^{20}	1.1550	1.1532
Per cent Yield	6.1%	7.4%

From the physical properties of ethyl chloroacetate listed in table I it was concluded that this fraction was unreacted ester.

---

[23] Beilstein, Handbuch der Organische Chemie, 4th Ed., Vol.2, p.198

The fraction which boiled at 77.5°C at 17 mm. had the following physical properties after purification by washing and distilling:-

Boiling point at 17 mm. -------- 77.5°C

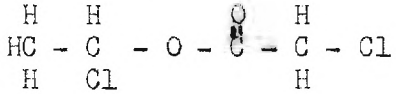
Color ---------- water clear

Odor ---------- pleasant

	Batch 2A		Batch 3	
n_D^{20}	1.4478		1.4472	
D_4^{20}	1.3149		1.3142	
	Calc'd for Dichloro Comp.	Found	Calc'd for Dichloro Comp.	Found
M_D	32.24	31.97	32.24	31.9
%Cl	45.50	45.30	-----	----
% Yield	29%		38.8%	

This compound reacted with concentrated ammonium hydroxide to give chloroacetamide, melting point 119°C, thus proving that it was a chloroacetate.

Since the chlorine analysis showed the compound contained 2 chlorine atoms to the molecule and the chloroacetamide showed that it was a chloroacetate, and since β chloroethyl chloroacetate had been shown to be present, the only remaining possible structure is that of α chloro ethyl chloroacetate whose structure is:-



chloroethyl chloroacetate is not listed in the literature.

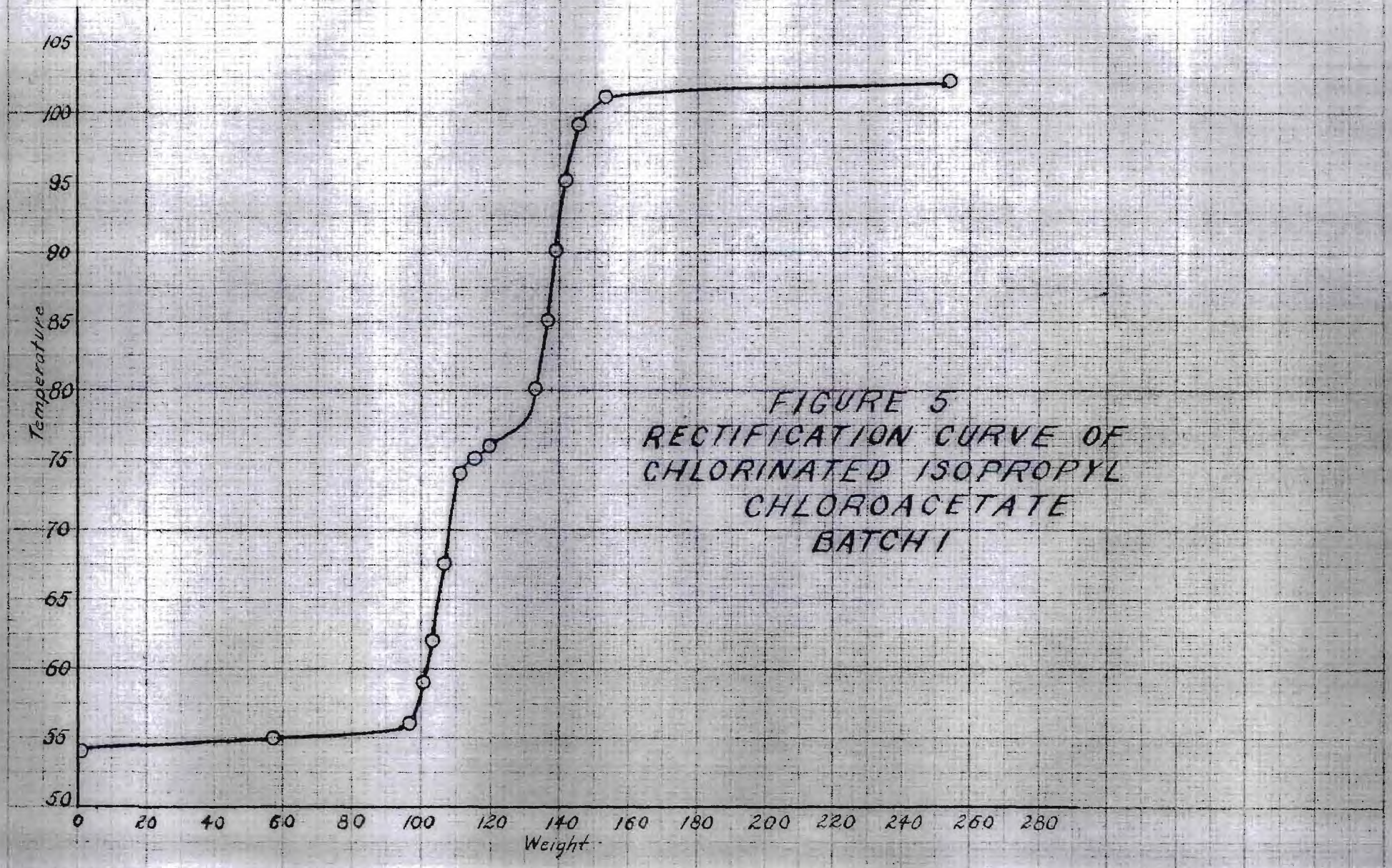


FIGURE 5
RECTIFICATION CURVE OF
CHLORINATED ISOPROPYL
CHLOROACETATE
BATCH I

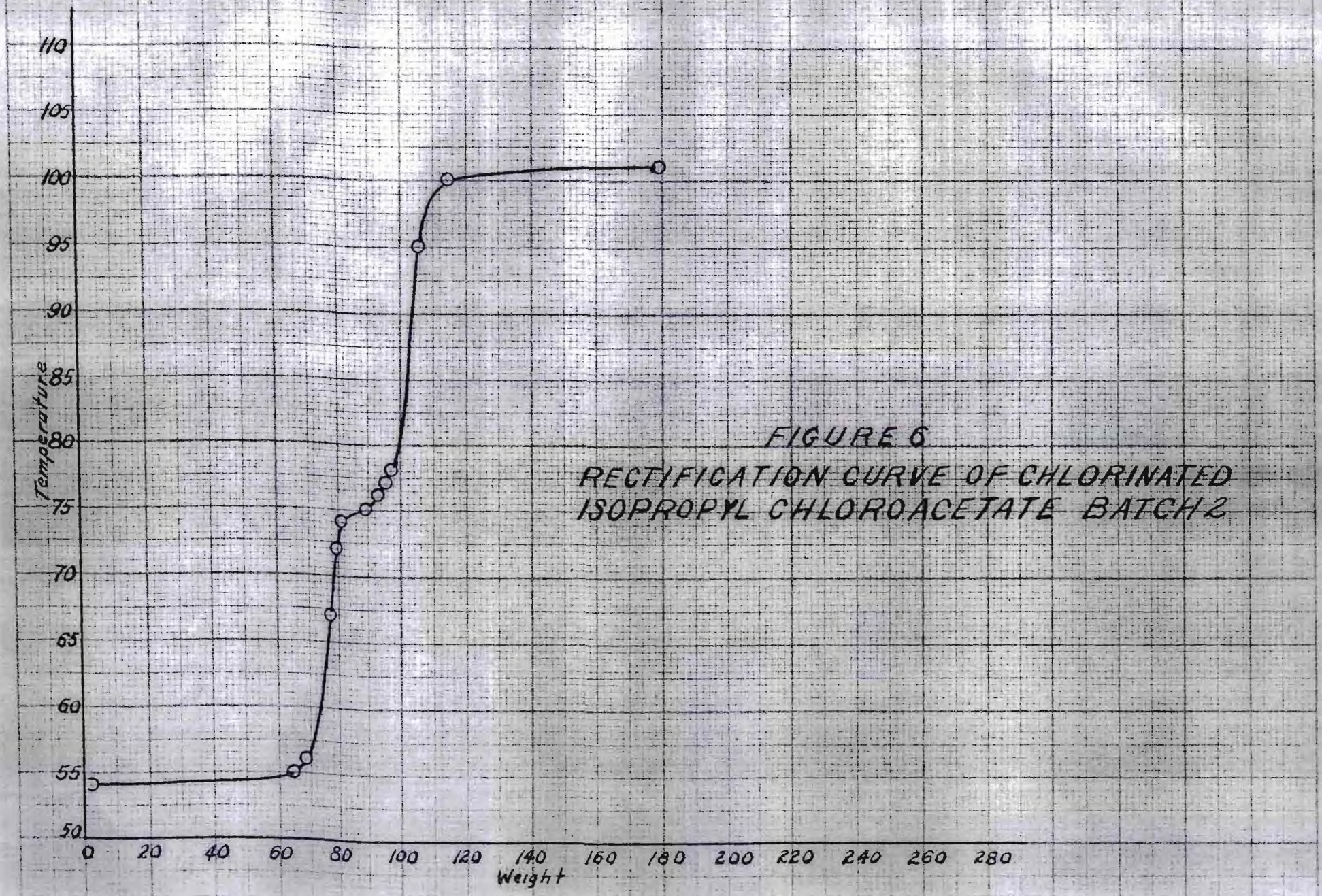


FIGURE 6
RECTIFICATION CURVE OF CHLORINATED ISOPROPYL CHLOROACETATE BATCH 2

PART V (D)

IDENTIFICATION OF THE PRODUCTS RESULTING FROM THE CHLORINATION OF ISOPROPYL CHLOROACETATE

Tables XVII and XVIII and figures 5 and 6 show that three main fractions are obtained on fractionating the chlorinated isopropyl chloroacetate. These main fractions had the following approximate boiling points:-

Highest boiling fraction ------- 101°C at 17 mm.

Next highest boiling fraction -- 77°C at 17 mm.

Lowest boiling fraction -------- 55°C at 17 mm.

The fraction which boiled at 55°C at 17 mm. had the following physical properties:-

	Batch 1	Batch 2
n_D^{20}	1.4199	1.4200
D_4^{20}	1.0867	1.0874

It was apparent from the physical properties of isopropyl chloroacetate listed in table I, that this fraction was unreacted isopropyl chloroacetate. The unreacted ester amounted to 34.7 per cent in batch 1 and 22.7 per cent in batch 2.

The fraction which boiled at 101°C had the following properties after purification:-

Color ------- water clear

Odor -------- sweet

Boiling point at 17 mm. --- 100°C

	Batch 1		Batch 2	
n_D^{20}	1.4563		1.4568	
D_4^{20}	1.2739		1.2743	
	Calc'd for Dichloro Comp.	Found	Calc'd for Dichloro Comp.	Found
M_D	36.84	36.18	36.84	36.56
%Cl	41.5	41.3	-----	-----
% Yield	20.2		22.4	

This compound reacted with concentrated ammonium hydroxide to give chloroacetamide, melting point 119°C, which showed that it was a chloroacetate. When the filtrate from the ammonium hydroxide treatment was continuously extracted with ether for about 10 hours and the ether distilled off, a residual liquid was obtained which, on fractionation, gave a liquid containing chlorine which had the following properties:-

Boiling point ------- 126-126.5°C

n_D^{20} ---------- 1.4379

D_4^{20} ---------- 1.1147

Heilbron[24] gives the following properties for 1-chloroisopropyl alcohol:-

Boiling point ------ 127°C

n_D^{20} ---------- 1.43924

D_{20}^{20} ---------- 1.115

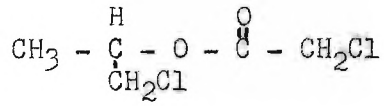
No solid derivatives are listed. The molecular refraction

---

[24] Heilbron, Dictionary of Organic Compounds, Vol.1, p.294 Oxford University Press (1934)

calculated for chloro isopropyl alcohol is 22.38. The experimental molar refraction was 22.25.

Since the compound gave chloro isopropyl alcohol and chloroacetamide, on treatment with ammonium hydroxide, the compound must have been chloro isopropyl chloroacetate whose structure is:-



Chloro isopropyl chloroacetate is not listed in the literature.

The fractions of batches 1 and 2 which boiled at approximately 77°C at 17 mm. had the following physical properties after redistillation:

Boiling point ---------- 75-76°C

Odor ---------- very sharp, penetrating

n_D^{20} ---------- 1.4870

D_4^{20} ---------- 1.4959

	Found
% Cl	61.3

From the above data this compound seemed to be a poly chloro derivative of decomposition product. It decomposed with water and reacted violently with ammonium hydroxide and sodium hydroxide.

All attempts to characterize the compound failed.

During the work with this compound a small amount was spilled on the arm. Even though it was immediately washed with water it produced a severe burn. The yield of this fraction was about 4 per cent in each batch.

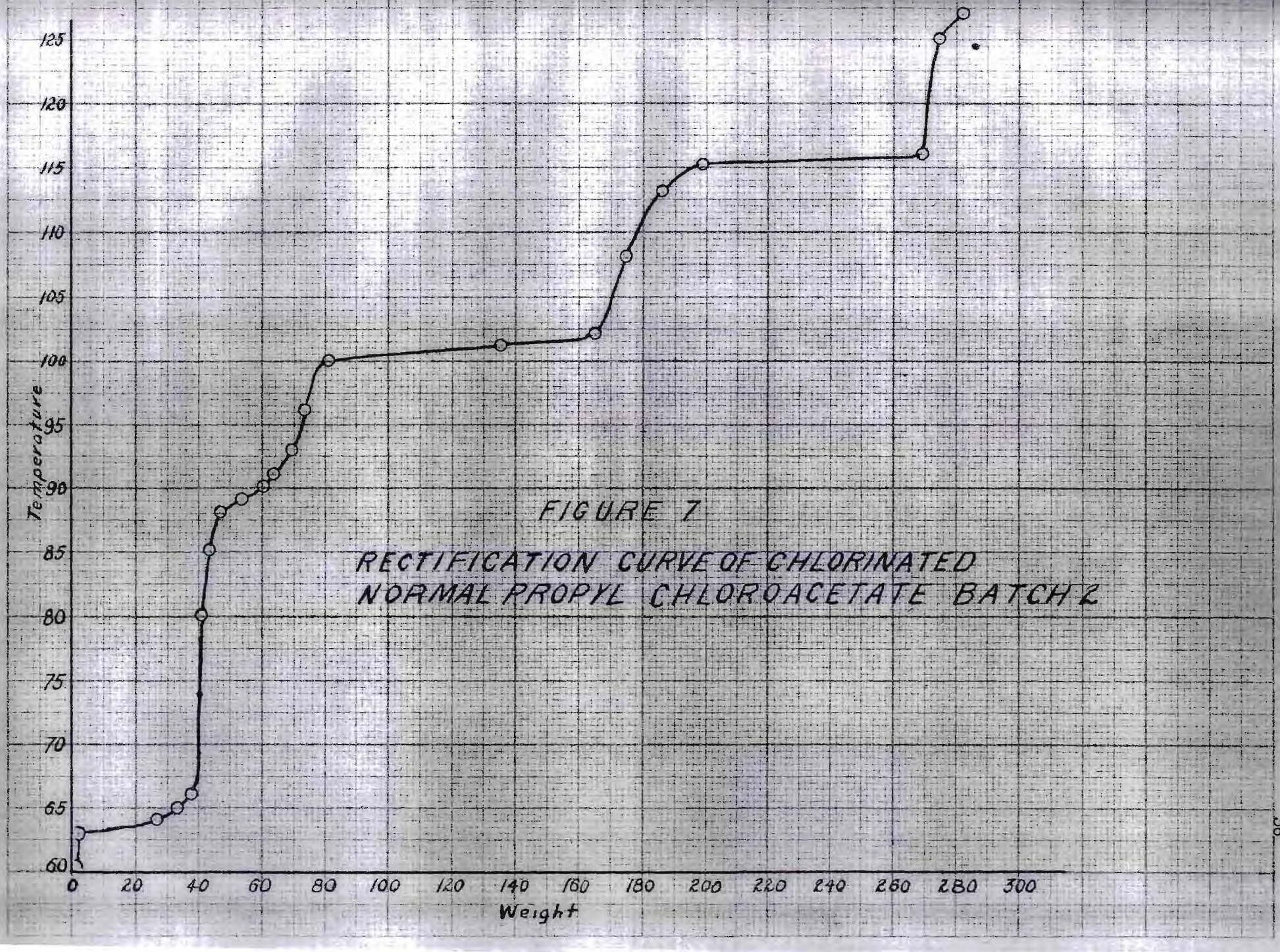
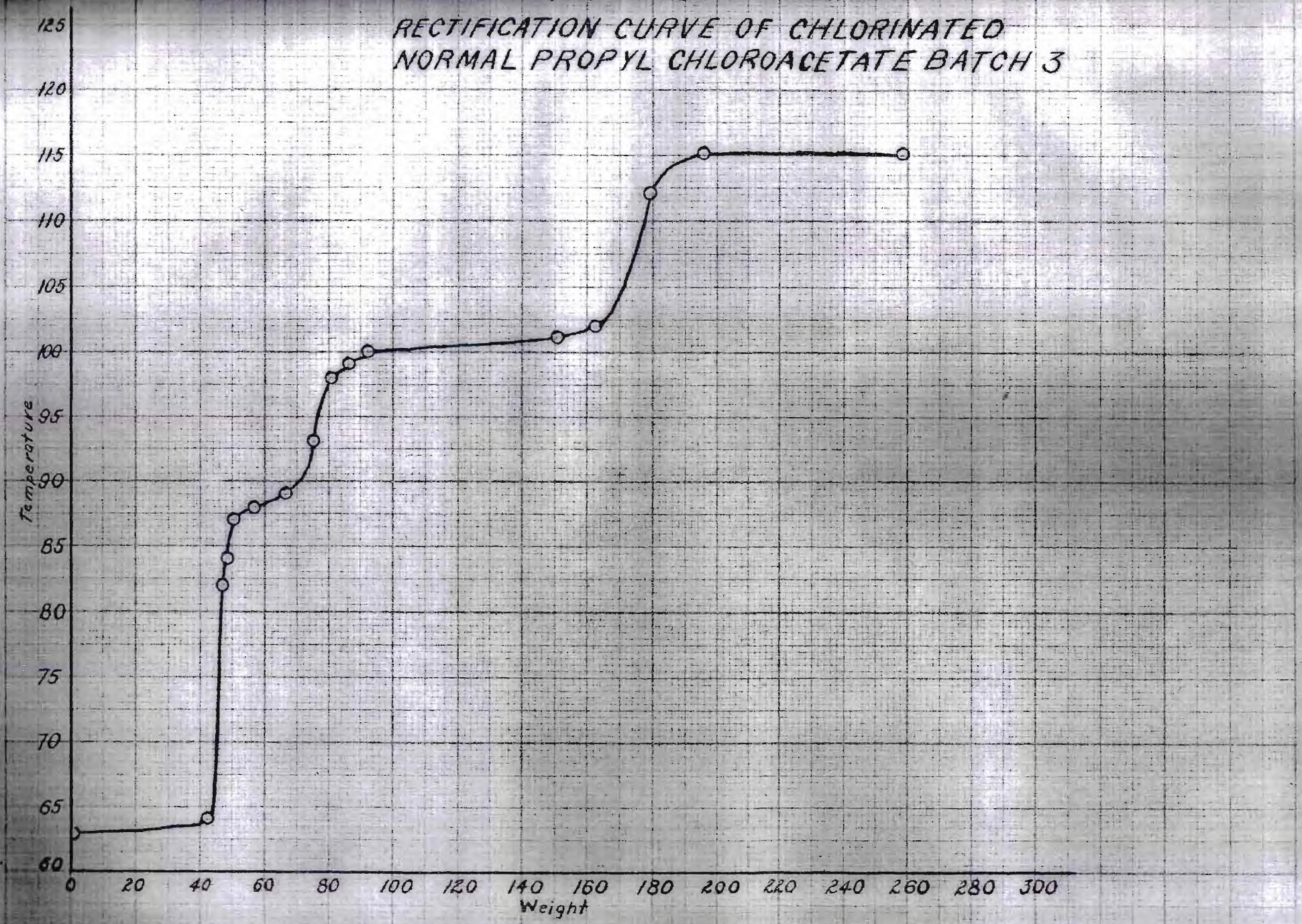


FIGURE 7

RECTIFICATION CURVE OF CHLORINATED NORMAL PROPYL CHLOROACETATE BATCH 2

FIGURE 8

RECTIFICATION CURVE OF CHLORINATED NORMAL PROPYL CHLOROACETATE BATCH 3



PART V (E)

PRODUCTS OBTAINED BY CHLORINATING NORMAL PROPYL CHLOROACETATE

A study of tables XIX and XX and figures 8 and 9 shows that 4 fractions result from the chlorination of normal propyl chloroacetate. These fractions have the following approximate boiling points at 17 mm.

Highest boiling fraction at 17 mm. ----- 115°C

Next highest boiling fraction ---------- 100°C

Next highest boiling fraction ---------- 88°C

Lowest boiling fraction at 17 mm. ----- 63°C

The fraction which boiled at 115°C had the following properties after purification:-

Boiling point at 17 mm. ------ 115°C

Color ------- water clear

Odor -------- sweet

	Batch 2		Batch 3	
n_D^{20}	1.4639		1.4639	
D_4^{20}	1.3054		1.3072	
	Found	Calc'd for Dichloro Compound	Found	Calc'd for Dichloro Compound
M_D	36.2	36.84	36.15	36.84
% Cl	---	-----	42.6	41.5
% Yield	20.8%		18%	

This compound reacted with concentrated ammonium hydroxide to give chloroacetamide which showed that it was a chloroacetate. The ether extract of the filtrate gave on fractionation a liquid, containing chlorine, which had the following properties:-

Boiling point ----- 160-161°C

D_4^{20} ---------- 1.1310

n_D^{20} ---------- 1.4466

Heilbron[25] lists the following properties for 3 chloro normal propyl alcohol:-

Boiling point ------ 161-162°C

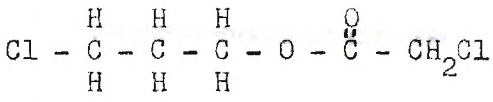
D_4^{20} ---------- 1.1309

n_D^{20} ---------- 1.44693

No solid derivatives are listed.

The calculated molar refraction for 3 chloro normal propyl alcohol is 22.38. The experimental value obtained was 22.35.

Since the compound reacted with ammonium hydroxide to give chloroacetamide and 3 chloro normal propyl alcohol, it follows that the compound was 3 chloro normal propyl chloroacetate whose structure is:-



There is no reference to 3-chloro normal propyl chloroacetate in the literature.

The fraction which boiled at 100°C at 17 mm. had the following properties after purification:-

Boiling point ----- 100°C

Color ---------- water clear

Odor ---------- slightly sweet, sharp

---

[25] Heilbron, Dictionary of Organic Compounds, Vol.1, p.322, Oxford University Press (1934)

	Batch 2	Batch 3
n_D^{20}	1.4567	1.4567
D_4^{20}	1.2793	------

	Calc'd for Dichloro Comp.	Found
M_D	36.84	37.56
%Cl	41.50	41.55
% Yield	24.6%	23.8%

This fraction reacted with concentrated ammonium hydroxide to give chloroacetamide, melting point 119°C, which shows that it was a chloroacetate. The ether extract of the filtrate gave on fractionation a liquid which contained chlorine and had the following properties:-

Boiling point ------ 132-133°C
n_D^{20} ---------- 1.4385
D_4^{20} ---------- 1.1101

Heilbron[26] gives the following properties for 2 chloro normal propyl alcohol:-

Boiling point ------- 133-134°C
D^{20} ---------- 1.103
n_D^{20} ---------- 1.43623

No solid derivatives are listed.

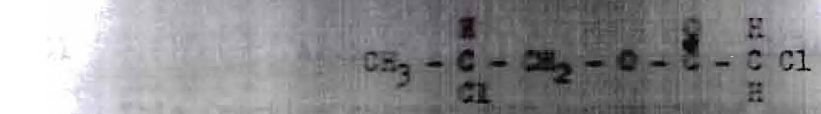
The experimental molar refraction was 21.9. The molar refraction calculated for 2 chloro normal propyl alcohol is 22.4.

Since the compound reacted with ammonium hydroxide to give 2 chloro

---

[26] Heilbron, Dictionary of Organic Compounds, Vol.I, p.322, Oxford University Press (1934)

normal propyl alcohol and chloroacetic, it follows that the compound was 2 chloro normal propyl chloroacetate whose structure is:-



2-chloro normal propyl chloroacetate is not listed in the literature.

The fraction which boiled at 63°C at 17 mm. had the following properties when purified:-

Boiling point ------- 64.5-65°C at 17 mm.

	Batch 2	Batch 3
D_4^{20}	1.1032	------
n_D^{20}	1.4252	1.4253

From the physical constants of normal propyl chloroacetate found in table I it was concluded that this fraction was unreacted ester. The unreacted ester amounted to 9 per cent in batch 2 and 19.4 per cent in batch 3.

The fraction of batches 2 and 3 which boiled at 88°C reacted slowly with water. When redistilled the compound had the following properties:-

Boiling point at 17 mm. ------ 88-89°C

Color ------ water clear

Odor ------- somewhat like propioaldehyde

D_4^{20} ------- 1.2573

n_D^{20} ------- 1.4491

	Calc'd for Dichloro Compound	Found
M_D	36.24	36.50
% Cl	41.5	41.14

This fraction reacted with concentrated ammonium hydroxide to give chloroacetamide, melting point 119°C, thus showing that it was a chloroacetate.

Since the chlorine analysis showed that 2 chlorine atoms were present in the molecule, and since the 3 chloro normal propyl chloroacetate and the 2 chloro normal propyl chloroacetate have already been shown to be present, the only remaining possibility is 1 chloro normal propyl chloroacetate whose structure is:-

$$CH_3 - CH_2 - \underset{Cl}{\overset{H}{C}} - O - \overset{O}{\overset{\|}{C}} - CH_2Cl$$

There is no reference to 1-chloro normal propyl chloroacetate in the literature. It was produced in 6.6 per cent yield in batch 2 and a 4.5 per cent yield in batch 3.

PART VI

CONCLUSION

At the start of this investigation it was thought that chlorination would take place at every possible position. No dichloroacetates were isolated, however. Since no dichloroacetates were isolated, the major part of the chlorine which reacted with the ester reacted either by chlorinolysis or by substitution on the alcohol radical of the ester.

For a study of the substitution reactions it was desirable to know the relative rates of reaction of primary and secondary hydrogen atoms. These were determined in the following manner:-

An inspection of the structure of normal propyl chloroacetate shows seven hydrogen atoms present on the alcohol radical of the molecule.

$$\overset{3}{CH_3} - \overset{2}{CH_2} - \overset{1}{CH_2} - O - \overset{O}{\overset{\|}{C}} - CH_2Cl$$

These hydrogen atoms are divided into types 1, 2 and 3 corresponding to carbon atoms number 1, 2, and 3 in the above structure. Assuming that all seven hydrogens react at the same rate, and since there are 2 hydrogens each on carbon atoms 1 and 2, and 3 hydrogen atoms on carbon atom 3, the yields of monochloro substitution products per mole of chlorinated ester would be:-

For substitution on carbon atom #1 ----- 2/7 mole or 28.5%

For substitution on carbon atom #2 ----- 2/7 mole or 28.5%

For substitution on carbon atom #3 ----- 3/7 mole or 42.8%

The actual average yields per mole of reacted ester, however, were:-

For substitution on carbon atom #1 ----- 6.4%

For substitution on carbon atom #2 ----- 28.7%

For substitution on carbon atom #3 ----- 22.5%

These yields show qualitatively that the reaction rates of the hydrogen atoms are type 2 > type 3 > type 1.

The relative rates of reaction of the different types hydrogen atoms were based on the rate of reaction of the primary hydrogens as unity. These relative rates were obtained as follows:-

The ratio of the yield of product where substitution occured on carbon #2 to the yield of product where substitution occured on carbon #3 (primary carbon) is 28.7/22.5, but since there are 3 hydrogen atoms on carbon #3 compared to 2 hydrogen atoms on carbon #2 the relative ratio is 28.7/22.5 x 3/2 or 1.9.

Then considering carbons 3 and 1 the ratio is 6.4/22.5 x 3/2 or .43.

The rates of substitution then are α hydrogens - .43, β hydrogens 1.9, and γ hydrogens 1 where the rate of substitution of the γ hydrogen atom is taken as unity.

By applying the same method to the chloronation of ethyl chloroacetate the rate of substitution of α hydrogen compared to the rate of substitution of β hydrogens as unity was 2.7.

Since methyl chloroacetate and isopropyl chloroacetate yielded only one product which was identified, no relative substitution rates were obtained for these esters.

PART VII

SUMMARY

1. The methyl, ethyl, isopropyl, and normal propyl esters of monochloroacetic acid have been chlorinated at 120°C.

2. Some chlorinolysis occured during chlorination, since a small amount of chloroacetyl chloride was produced during each chlorination.

3. The main substitution reactions occured on the alcohol part part of the ester since no dichloroacetates were isolated.

4. The approximate relative rates of substitution at 120°C of the α, β, and γ hydrogen atoms of normal propyl monochloroacetates and of the α and β hydrogen atoms of ethyl chloroacetate have been determined. These rates for normal propyl chloroacetate are, α hydrogens- .43, β hydrogens 1.9, and γ hydrogens 1. where the γ hydrogen rate is unity. The approximate rate of substitution of the α hydrogens of ethyl chloroacetate compared to the rate of the β hydrogens as unity is 2.7.

5. One mole of methyl chloroacetate when chlorinated at 120°C, gives approximately .65 mole of chloro methyl chloroacetate as the major product. A small amount of chloroacetyl chloride was also produced.

6. One mole of ethyl chloroacetate on chlorination at 120°C, gives in addition to a small amount of chloroacetyl chloride, approximately .07 mole of unreacted ethyl chloroacetate, .34 mole of 1 chloro ethyl chloroacetate, and .18 mole of 2 chloro ethyl chloroacetate.

7. One mole of isopropyl chloroacetate on chlorination at 120°C, gives approximately .29 moles of unreacted isopropyl chloroacetate, .21 mole of chloro isopropyl chloroacetate, and 4 per cent of a compound which was not identified, in addition to a small amount of chloro acetyl

chloride.

8. One mole of normal propyl chloroacetate on chlorination gives approximately .14 moles of unreacted normal propyl chloroacetate, .055 mole of 1-chloro normal propyl chloroacetate, .22 mole of 2-chloro normal propyl chloroacetate, and .24 mole of 3-chloro normal propyl chloroacetate in addition to a small amount of chloroacetyl chloride.

9. The following compounds, not listed in the literature, have been prepared and their physical properties determined:

A. 1-chloro ethyl chloroacetate, page 30

$$CH_3 - CH_2Cl - O - \overset{O}{\overset{\|}{C}} - CH_2Cl$$

Boiling point at 17 mm. -- 77.5°C

n_D^{20}------ 1.4475

D_4^{20}------ 1.3145

B. Chloro isopropyl chloroacetate (pp.33-34)

$$CH_3 - \underset{CH_2Cl}{\overset{H}{C}} - O - \overset{O}{\overset{\|}{C}} - CH_2Cl$$

Boiling point at 17 mm. -- 100°C

n_D^{20}------ 1.4565

D_4^{20}------ 1.2741

C. 1-chloro normal propyl chloroacetate (p.41)

$$CH_3 - CH_2 - CHCl - O - \overset{O}{\overset{\|}{C}} - CH_2Cl$$

Boiling point at 17 mm. -- 88-89°C

n_D^{20}------ 1.4491

D_4^{20}------ 1.2573

D. 2-chloro normal propyl chloroacetate (p.40)

$$CH_3 - CHCl - CH_2 - O - \overset{O}{\overset{\|}{C}} - CH_2Cl$$

Boiling point at 17 mm. -- 100°C

n_D^{20} ------ 1.4567

D_4^{20} ------ 1.2793

E. 3-chloro normal propyl chloroacetate

$$CH_2Cl - CH_2 - CH_2 - O - \overset{O}{\overset{\|}{C}} - CH_2Cl$$

Boiling point at 17 mm. -- 115°C

n_D^{20} ------ 1.4639

D_4^{20} ------ 1.3058

BIBLIOGRAPHY

Adkins, McElvain and Klein, Practice of Organic Chemistry, 3rd Ed., McGraw Hill (1940)

Beilstein, Hanbuch der Organischen Chemie, 4th Ed., Vol.II

Gayler, Geogia School of Technology, Master of Science Thesis (1940)

Hass and Marshall, Ind. Eng. Chem., 23, 352 (1931)

Hass, McBee and Weber, Ind. Eng. Chem., 29, 1190 (1935); 28, 333 (1936)

Hass and Weber, Ind. Eng. Chem., Anal. Ed., 7, 231 (1935)

Hass, McBee and Hatch, Ind. Eng. Chem., 29, 1335 (1937)

Heilbron, Dictionary of Organic Compounds, Oxford University Press (1938)

Kamm, Qualitive Organic Analysis, 2nd Ed., John Wiley and Sons (1938)

McKenny, Ind. Eng. Chem., Anal. Ed., 6, 258 (1934)

Morton, Laooratory Technique in Organic Chemistry, McGraw Hill (1938)

Rudy and Fugassi, Ind. Eng. Chem., Anal. Ed., 12, 757 (1940)

Shriner and Fusion, Identification of Organic Compounds, 2nd Ed., John Wiley and Sons (1940)

Smiles, The Relation Between Chemical Constitution and Some Physical Properties, Longmans, Green and Co. (1919)

Stepanow, Ber., 39, 4056 (1906)

Waddle and Adkins, J. Am. Chem. Soc., 61, 3361 (1939)